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Synthesis and Study at a Solid/Liquid Interface of Porphyrin Dimers Linked by Metal Ions

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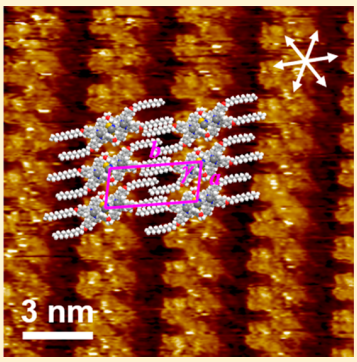
Supporting Information

ABSTRACT: Several porphyrin dimers linked by metal ions were prepared. One trimeric compound was also isolated and one porphyrin dimer linked by palladium(II) could be structurally characterized. In solution, the size of the new compounds was estimated by DOSY NMR techniques. These compounds all contained long aliphatic chains (O–$C_{12}H_{25}$), which were used to assemble them at a highly oriented pyrolytic graphite (HOPG)/liquid interface. The highly ordered arrays were visualized by scanning tunneling microscopy (STM).

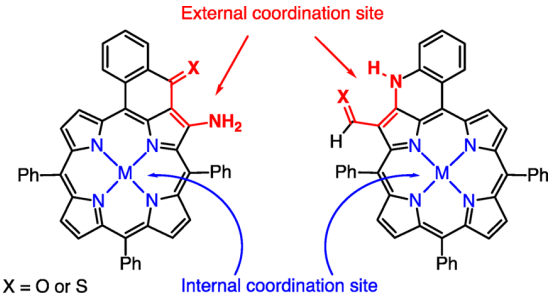


INTRODUCTION

To build molecular scale devices on surfaces, it is essential to control the organization of the molecules at the surfaces or at the solid/liquid interface.[1] Self-assembly is often used as an organizational tool, resulting in nice structures on various substrates.[2] Molecules like porphyrins, chlorins, or corroles are ubiquitous molecules and are in the center of numerous essential processes found in living systems. Tetrapyrrolic macrocycles are found in many light-harvesting complexes and in photosynthetic reaction centers because of their exceptional optical properties. These properties were recognized quite early by synthetic chemists and therefore these molecules were modified and designed to offer new interesting optical, electrochemical, photochemical, and chemical properties.[3] Because of these properties, it was obvious that these molecules should be studied at the solid/liquid interfaces. Until now, several authors have shown that porphyrins could be assembled on HOPG or metal surfaces.[4] The STM technique was used to visualize single molecules on the surface, thus acting as a well-known characterization tool for large molecules.[5] In addition, STM demonstrated how these molecules form highly ordered assemblies on these substrates.[6] We have shown earlier that metallo-porphyrins could be connected by coordination bonds if the aromatic core of the macrocycle was functionalized with an external chelating coordination site (see Chart 1).[7]

The external chelate was coplanar and conjugated with the aromatic core, allowing electronic delocalization between two porphyrins linked by metal ions.[8] This electronic delocalization was extended to oligoporphyrins by using monomeric porphyrins bearing two external coordination sites.[9] Electronic communication through the coordination linkage between the individual macrocycles was demonstrated. More recently, we have shown that this electronic delocalization was responsible for ultrafast energy transfer from a zinc(II) porphyrin to a free base porphyrin linked together by a palladium(II) or platinum(II) ion.[10] In this study, we have modified our initial porphyrins by adding alkyl chains at the periphery of these molecules and attempted to organize and assemble them on a HOPG surface.

Chart 1. Porphyrins Bearing External Coordination Sites



RESULTS AND DISCUSSION

Monomeric compounds bearing long aliphatic chains in addition to external coordination sites were the first synthetic

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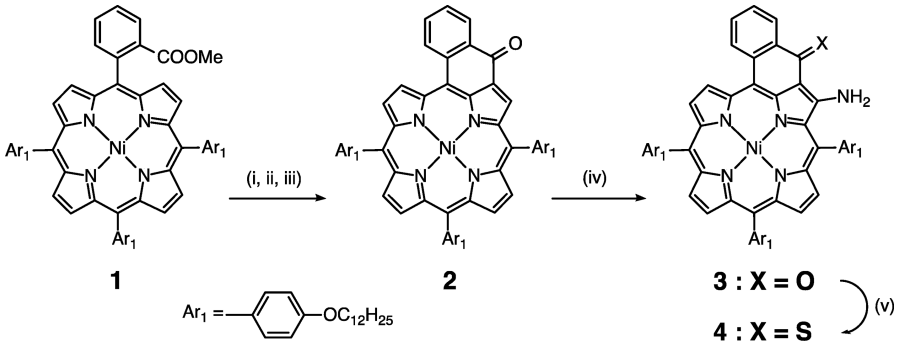
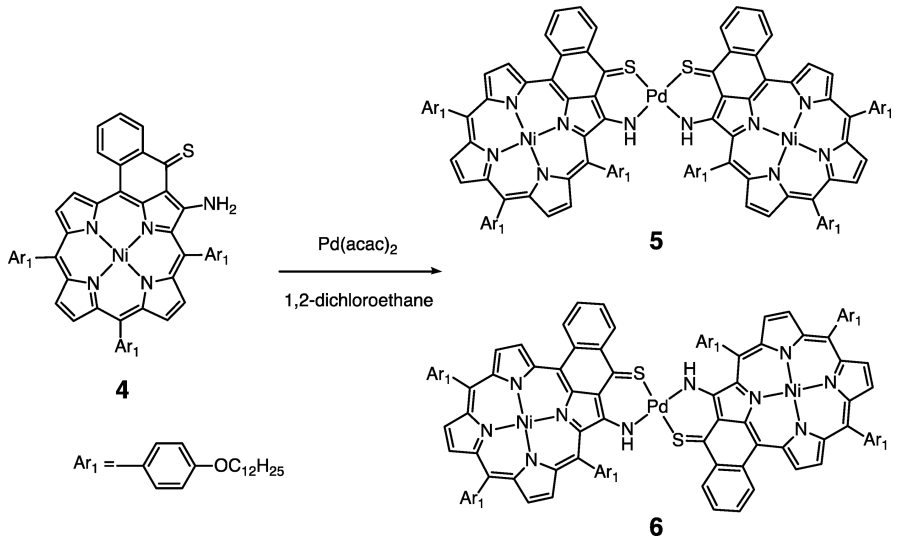
Scheme 1. Preparation of the Starting Porphyrins 2−4[a]



[a](i) LiOH, dioxane/water (ii) $(COCl)_2$, toluene (iii) $SnCl_4$, toluene (iv) 4-amino-4*H*-1,2,4-triazole, NaOH, toluene/EtOH (v) Lawesson's reagent, toluene, 80 °C.

Scheme 2. Preparation of Porphyrin Dimers 5 and 6



goal. The arylalkylether meso group (Ph-$OC_{12}H_{25}$) was chosen to obtain porphyrin monomers suitable for deposition at a HOPG liquid/surface interface. The preparation of porphyrins bearing enamino(thio)ketones as external coordination sites is well established.[9] The starting porphyrin with three *meso*-alkoxyaryl groups and one *ortho*-carbomethoxyphenyl group was obtained via a classical statistical Lindsey procedure.[11] After hydrolysis of the ester group, intramolecular Friedel−Crafts cyclization gave the extended nickel porphyrin **2**. Then, amination with the Katritsky reagent[12] gave **3** and thionation with Lawesson's reagent[13] led to the desired nickel porphyrin **4** bearing one external coordination site and three aliphatic tails (see Scheme 1).

Nickel porphyrin **4** was then reacted with palladium(II) to prepare the expected dimer. To our surprise, and contrary to previous results, we observed the formation of two new compounds with almost the same retention time on TLC (see Scheme 2). We could not separate them, but the ^{1}H NMR of the isolated mixture of the two compounds clearly indicated the presence of the two square planar isomeric dimers **5** and **6** (cis and trans coordination geometry around the linking palladium-(II) ion). This was particularly visible for the aliphatic alkoxy chains: some CH_2 protons are found diastereotopic due to the chirality of the *cis* isomer and the chemical shifts of several CH_2 protons were unusually upfield due to the ring current effect of the other porphyrin in the dimer (chemical shift close to 0 ppm)(see Figure 27). Both isomers were observed previously, but only for porphyrins bearing external enaminoaldehydes.[8c] Here, the steric hindrance of two Ar_1 meso groups was not large enough to prevent the formation of the *cis* isomer **5**, in contrast to the 3,5-*t*-Bu_2-phenyl groups used previously.[8b] However, by refluxing overnight a dichloroethane solution of the isolated mixture of the two isomers **5** and **6**, the initial cis/trans mixture was cleanly converted to the single trans isomer **6** as shown by ^{1}H NMR (see Figure 1).

Reacting porphyrin **4** with an excess of $Pd(acac)_2$ gave, although in rather moderate yield (40%), porphyrin **7** bearing a palladium acetylacetonate group on the external coordination site. During this reaction, the porphyrin dimers **5** and **6** was also isolated as side product in 34% yield (see Scheme 3). Even with a large excess of Pd(II) and by adding the porphyrin solution dropwise to the Pd(II) solution, the external soft chelate of porphyrin **4** reacted rapidly with the soft Pd(II) ion to afford also dimers **5** and **6**.

Until now, we were unable to prepare a nickel porphyrin bearing two external coordination sites and two Ar_1 *meso* groups. Therefore, we prepared dimers and trimers by using an unsymmetrical bis-functionalized nickel porphyrin monomer **8** previously described.[9b] During the course of this work, we obtained single crystals of **8** and the structure was solved (see

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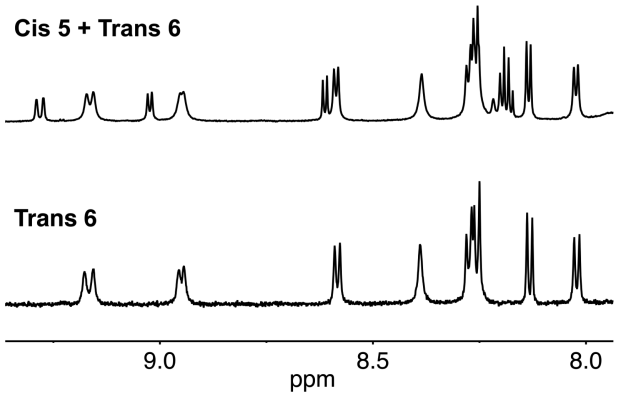


Figure 1. ^{1}H NMR of the mixture of porphyrin dimers **5** and **6** (top spectrum) and of dimer **6** after heating in dichloroethane (pyrrolic region).

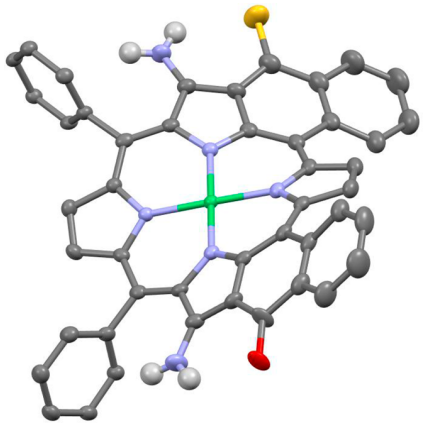


Figure 2. X-ray structure of porphyrin **8**. All hydrogen atoms (except those involved in H-bonds) and the *tert*-butyl groups are omitted for clarity.

f2 Figure 2). The coordination geometry of the central nickel(II) is almost square planar with Ni−N bond lengths around 1.91 Å. These rather short metal−nitrogen bonds and the presence of two additional fused aryl groups cause the distortion of the porphyrin ring, which is highly ruffled. For the two external coordination sites (N−O and N−S), intramolecular and intermolecular hydrogen bonds were found between N−H and C═O (or C═S).

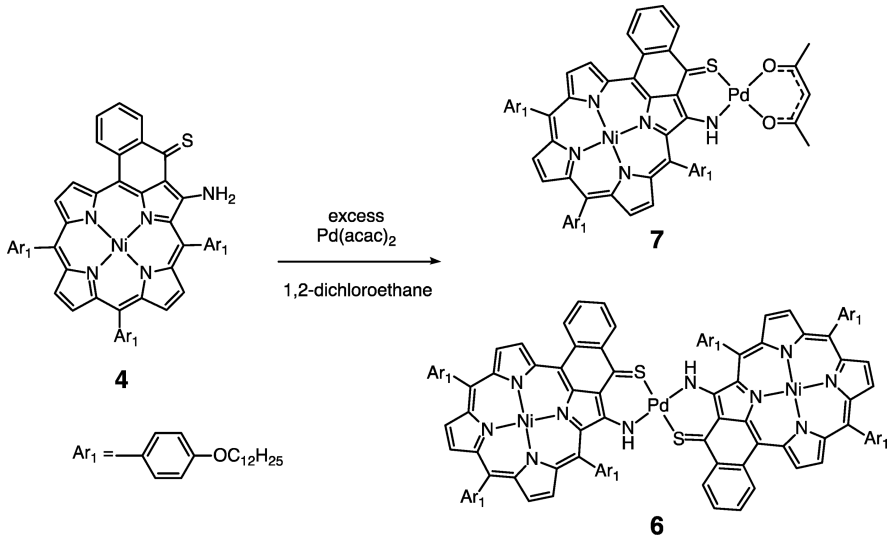
By reacting **4**, **8** and palladium(II), a complex mixture of products was obtained, but most of them were isolated cleanly s4 (see Scheme 4). As expected, the mixture of dimers **5** and **6** was isolated once again, along with the heterodimer **9** bearing one external coordination site and the symmetrical dimer **10**, which bears two external coordination sites.

Thionation of the external coordination site of **9** with Lawesson's reagent gave dimer **11**, which bears now an external s5 N−S coordination site (see Scheme 5).

By reacting **11** with 0.5 equiv of palladium(II), we expected to obtain a porphyrin tetramer. The formation of oligomers was indeed observed, but we were not able to separate the trimer **14** (vide infra) from the expected tetramer. The presence of both compounds was easily demonstrated by MALDI mass spectrometry, but was difficult to deduce from the ^{1}H NMR spectrum alone, because almost all signals from the two compounds are superimposed due to very similar chemical environment. Despite the good stability of the palladium(II) linkage, this strategy was unsuccessful due to partial decoordination of the two porphyrins belonging to **11** and then reaction to afford simultaneously trimer **14** and a tetramer. Moreover, we noticed in a qualitative way that the amount of trimer **14** found in the mixture of oligomers increased with longer reaction times, indicating that **14** was probably one of the thermodynamic sinks of the reaction. Another synthetic strategy was then envisaged. The porphyrin dimer **10** was first treated with the Lawesson's reagent to afford the new porphyrin dimer **12**, now bearing two external enaminothioketone coordination sites. s6

Reaction of this dimer **12** with two equivalents of the functionalized porphyrin **7** gave again a mixture of products, namely trimer **14** and a tetramer together with recovered starting material. Single crystals of dimer **12** were obtained and its X-ray structure represents the first structure of a porphyrin dimer of this type. The porphyrins were extremely distorted due to the very short Ni−N bond lengths (1.90 Å or less) and to the presence of additional aromatic rings fused to the f3

Scheme 3. Preparation of Porphyrin 7



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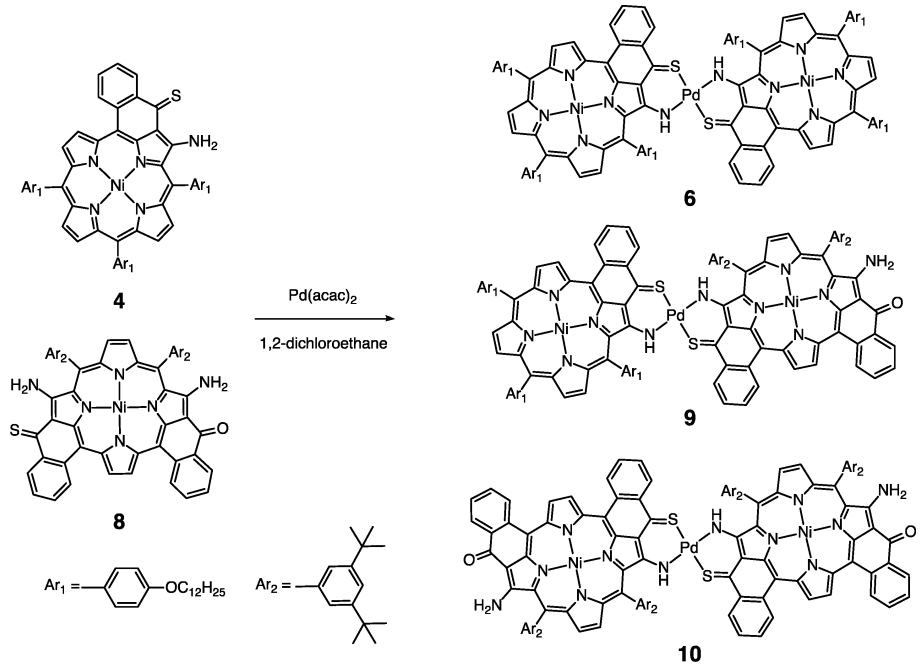
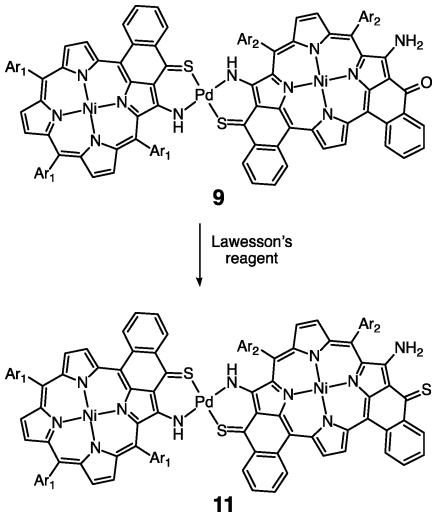
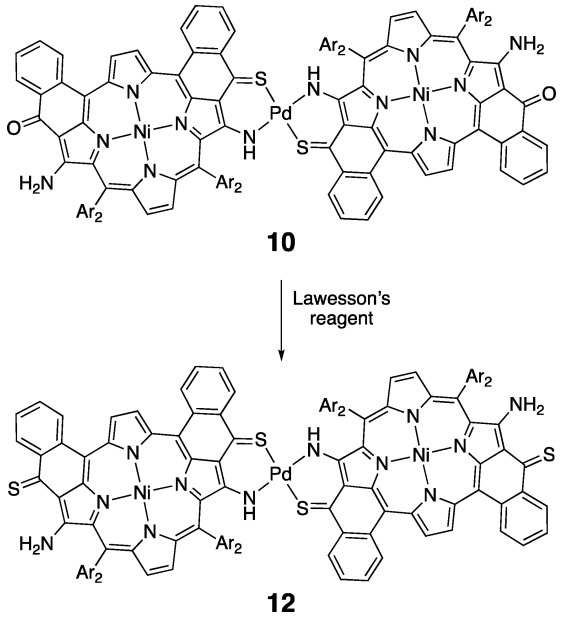
Scheme 4. Preparation of Porphyrin Dimers 6, 9, and 10



Scheme 5. Preparation of Porphyrin Dimer 11 by Thionation of 9



Scheme 6. Preparation of Porphyrin Dimer 12 by Thionation of 10



porphyrin core (see Figure 3). The coordination geometry around the linking palladium(II) is trans square planar and the Pd−S and Pd−N lengths are close to 2.3 and 2 Å, respectively. The three fused rings bearing the external coordination sites are almost planar and the geometry around the palladium(II) ion renders the two planes belonging to two different porphyrins almost coplanar. However, within a given porphyrin, the angle between the planes of the three fused rings are approximately 65°. In monomeric porphyrins, these angles are similar (see Figure 2 for compound **8** or ref 9b for a related structure). These angles being additive in dimer **12**, the overall observed distortion between the two external sites is close to 130°.

The presence of trimer **14** in all reactions incited us to try to prepare it deliberately, because trimer **14** was always present in all attempts. The reaction of porphyrin **7** with the previously described bis-functionalized porphyrin **13** gave cleanly trimer **14** in 77% yield (see Scheme 7). No tetramer was detected in the MALDI mass spectrum and the very clean ^{1}H NMR spectrum recorded at 50 °C confirmed this (see Figures 85 and 86).

The electronic spectra of the different porphyrins were recorded and confirmed earlier findings that by extending the length of the molecule bathochromic shifts were present. In Figure 4 are shown the spectra of monomer **4**, dimer **6**, and trimer **14**. It can be easily recognized that electronic delocalization, leading to bathochromic shifts, is again observed in these new compounds. Comparison of the electronic spectra of dimer **6** and trimer **14** shows that the spectrum of **14** is not

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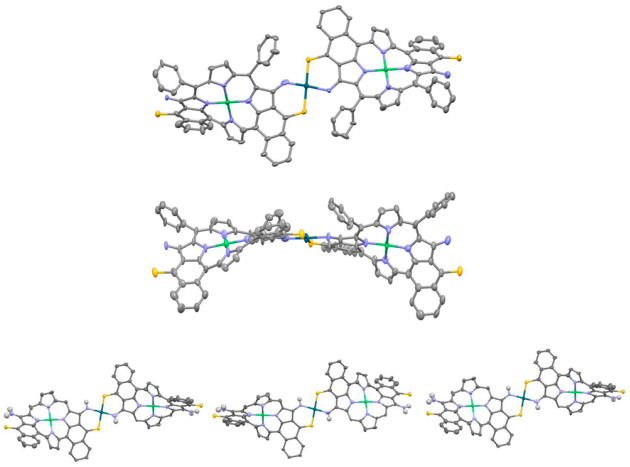
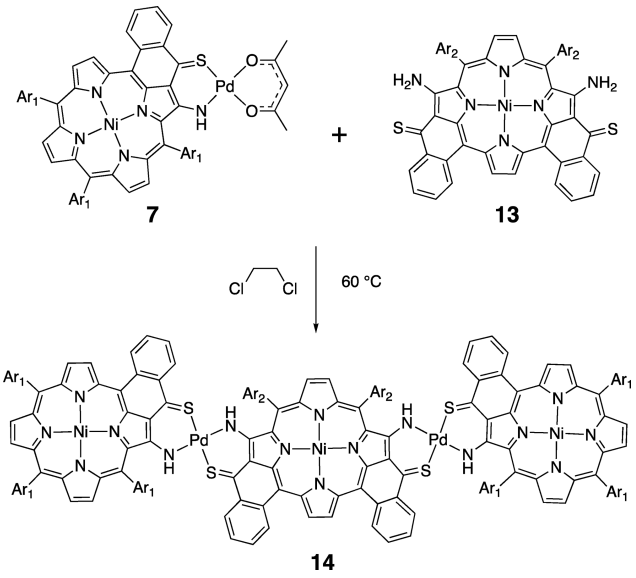


Figure 3. (a) Top: Two views of the X-ray structure of porphyrin dimer **12**. Five chlorobenzene solvent molecules, all hydrogen atoms and the *tert*-butyl groups are omitted for clarity. (b) Bottom: View showing the infinite dimer chains maintained together by intermolecular hydrogen bonds between the external enaminothioketone sites (chlorobenzene solvent molecules, *meso*-aryl groups and all hydrogen atoms, except the NH, are omitted for clarity).

Scheme 7. Preparation of Porphyrin Trimer 14



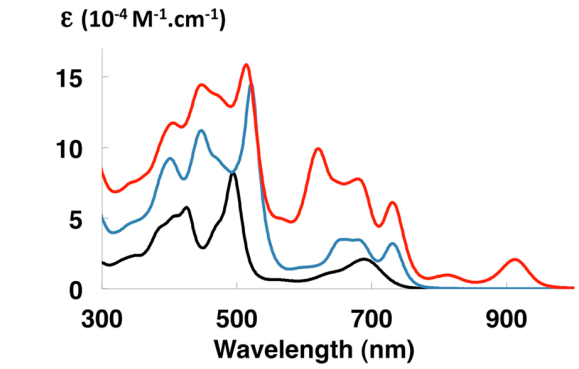


Figure 4. Electronic absorption spectra of porphyrin **4** (in black), dimer **6** (in blue), and trimer **14** (in red).

the simple addition of the spectra of dimer **6** (λ_{max} = 730 nm) and porphyrin **13** (λ_{max} = 772 nm). Strong interactions between the three subunits clearly add additional electron delocalization through the connecting metal ions' d orbitals and lead to the observed bathochromic shift (λ_{max} = 913 nm).

These compounds were characterized by standard spectroscopic techniques (NMR, mass, electronic spectra). To obtain additional information about the size and to show that dimers or the trimer were pure compounds and not a mixture of oligomeric species in solution, we used DOSY NMR techniques to determine the diffusion coefficients of the different isolated compounds.[14] The molecular volume, closely related to the translational self-diffusion coefficient, was assumed to be similar to a sphere. Indeed, the values obtained for some compounds (listed in Table 1) were in good agreement with the size estimated from previous X-ray data.[7−9]

Table 1. NMR DOSY Data for Compounds 6, 7, 11, and 14

compound	self-diffusion Coefficient ($\mu m^2/s$)	calculated volume (as a sphere) (nm^3)	estimated dimensions (nm) (l x w x h = volume)
6	296	10.7	5.4 × 3.0 × 0.7 = 11.3 nm^3
7	384	4.9	2.6 × 3.0 × 0.7 = 5.5 nm^3
11	336	7.3	3.6 × 3.0 × 0.8 = 8.6 nm^3
13	253	17	7.0 × 3.0 × 0.9 = 18.9 nm^3

Our initial goal was to test the possibility of assembling these molecules on HOPG surfaces. Several compounds were tested at a solid/liquid interface consisting of HOPG and a 1-phenyloctane solution of the compound. Unfortunately, the trimeric compound **14** did not assemble neatly on the surface. However, monomer **4**, and dimers **6** or **11** gave very nice patterns, as shown in Figure 5. Bright spots represent the porphyrin core, whereas dark troughs are composed of dodecyloxy chains. Plausible molecular models are superimposed on each STM image. The vacant spaces between the alkyl chains (Figure 5c, 5d and 5e) may be filled with the coadsorbed solvent molecules.[15]

The crystallographic data from the STM images are listed in Table 2. The nickel porphyrin monomer **4** and trans dimer **6** were found in a centro-symmetric unit cell, as was the case for the trans dimer **11**. For compounds **4** and **6**, only two of the three tails per porphyrin were in van der Waals contact with the HOPG surface, and followed one of the HOPG lattice direction, implying that the third tail near the external coordination site is dangling in the solvent. The lattice constants of **6** were almost identical to those of **4** despite the presence of coordinating metal between the ligands in **6**. In the case of **11**, the porphyrin core was aligned in a manner similar to that of **4** and **6**. All the alkyl chains are attached along the HOPG lattice direction. Thus, porphyrin building blocks with an external coordination site could be assembled into well-ordered two-dimensional structures on a solid substrate.

CONCLUSION

In conclusion, these preliminary experiments have shown that the assembly of metallo-porphyrins bearing external coordination sites on surfaces like HOPG is indeed possible. Work is in progress to prepare porphyrins bearing two external coordination sites and two aliphatic tails with different lengths. With these porphyrins it should then be possible to self-assemble them around metal ions directly on the surface to obtain finite

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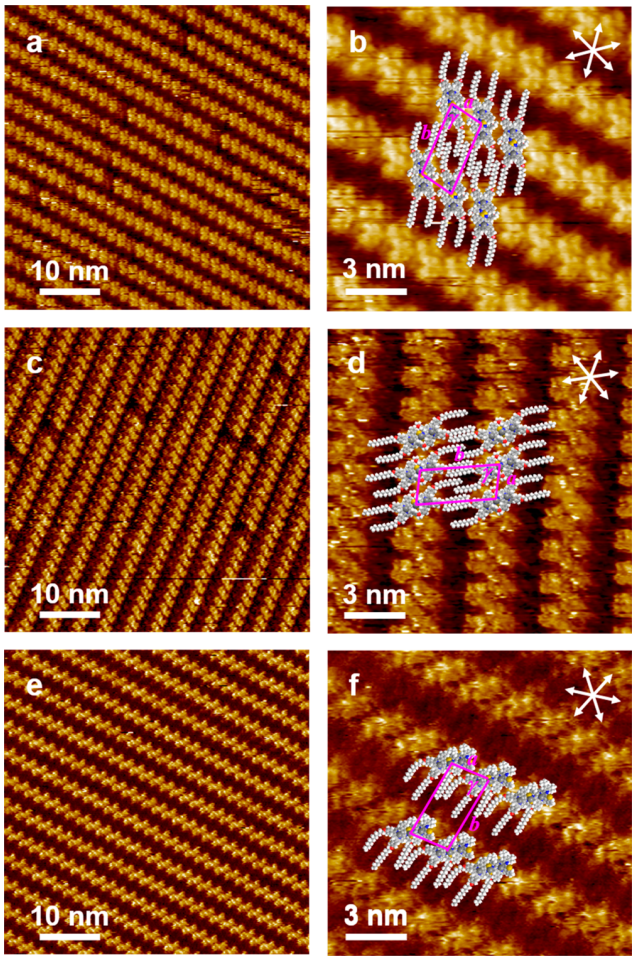

Figure 5. STM images of compounds **4** (a, b), dimer **6** (c, d), and dimer **11** (e, f) at the HOPG/1-phenyloctane interface. One of the three dodecyloxy chains was omitted in the molecular models in (b) and (d) because it was not attached on the HOPG surface. A set of arrows indicates the underlying HOPG lattice direction. Tunneling conditions: (a) I = 2.0 pA, V = −1118 mV; (b) I = 1.0 pA, V = −1210 mV; (c) I = 1.1 pA, V = −1027 mV; (d) I = 1.5 pA, V = −1000 mV; (e) I = 1.0 pA, V = −1088 mV; (f) I = 1.0 pA, V = −992 mV.

Table 2. Unit Cell Parameters Measured from STM Images

compound	a (nm)	b (nm)	γ (deg)
4	1.73 ± 0.13	3.57 ± 0.16	81 ± 4
6	1.79 ± 0.22	3.65 ± 0.20	83 ± 3
11	1.85 ± 0.18	3.72 ± 0.18	84 ± 5

or infinite linear porphyrin tapes with electron delocalization between all individual porphyrins.

EXPERIMENTAL SECTION

General. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400, 500, or 600 MHz using $CDCl_3$ as solvent. MALDI-TOF mass spectra were obtained using dithranol as matrix with a Bruker Autoflex II equipped with a 337 nm laser. UV−visible spectra were recorded on a CARY 5000 UV−vis−NIR spectrometer. Dichloromethane was distilled from calcium hydride and toluene from sodium/benzophenone ketyl. Chromatographic separations were performed with Merck TLC silica gel 60 F254 and Kieselgel Si 60 (40−63 mm) and gel permeation with Bio-Beads S-X1 from Bio-Rad. All MALDI mass spectra of the porphyrin monomers, dimers, and trimers are given in the Supporting Information. The mass spectral pattern for each compound is compared with the simulated spectrum. Measurement of self-diffusion coefficients were performed on a BRUKER 600 MHz spectrometer—Avance III, equipped with a Bruker BBI probe developing a pulsed field gradient of 5.1 G/cm/A. Diffusion NMR data were acquired at 298 K using a Stimulated Echo pulse sequence with smoothed square bipolar z gradients in 34 increments. The duration of half gradients were 1 ms and the diffusion time was optimized for each sample between 120 and 140 ms. A recycle delay of at least 4 s was respected between each scans. DOSY spectra were generated by the dedicated module of NMRNotebook software, using Inverse Laplace Transform (ILT) driven by maximum entropy.

STM Measurements. Two-dimensional structures of porphyrins with an external coordination site were visualized by using low-current STM (Nanoscope IIIa: Digital Instruments, CA) at HOPG/1-phenyloctane interface. Pt/Ir wire (90/10) was mechanically cut for a STM tip. The compounds were dissolved in 1-phenyloctane at a concentration ranging from 0.75 to 1 mM, and the solution was deposited on HOPG (ZYB grade, NT-MDT, Russia). The reproducibility of the STM images was checked by using different tips and samples. All STM images were obtained in the constant current mode, and analyzed with the SPIP software (Image Metrology, Denmark). The STM images were corrected by a HOPG lattice under the physisorbed monolayer.

Synthesis. The starting benzaldehyde derivatives (4-dodecyloxybenzaldehyde and 2-carbomethoxybenzaldehyde) were prepared using published procedures.[16,17] The nickel *meso*-tetraaryl porphyrin **1** with three dodecyloxy-phenyl and one phenyl-ester was obtained in 5 to 6% yield (overall yield for porphyrin synthesis followed by metalation with $Ni(acac)_2$) by using a procedure described previously for other benzaldehydes.[8b] The nickel porphyrins **8** and **12** with two external coordination sites were available.[9b]

Porphyrin ***2***. A solution of lithium hydroxide (150 mg, 3.6 mmol) and nickel porphyrin **1** (150 mg, 0.12 mmol) in dioxane/water (100 mL/5 mL) was refluxed under argon for 2 days. After evaporation of the solvents, the residue was filtered through a short silica gel column (eluent dichloromethane with 0.5% acetic acid). After evaporation and drying, the solid residue was taken up in toluene (100 mL), an excess of oxalyl chloride (5 mL) added, and after 1 h of stirring, the solution was heated up and the unreacted excess oxalyl chloride eliminated by distillation. After the mixture was cooled to RT, tin(IV) tetrachloride (1 mL) was added. After 0.5 h of stirring, dichloromethane (150 mL) was added and the reaction was quenched with an aqueous sodium hydroxide solution (5%). The organic phase was washed several times with water and dried over sodium sulfate. After evaporation of the solvents, the desired compound **2** was obtained in 87% yield by precipitation from dichloromethane/methanol (127 mg, 0.102 mmol). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ_H 9.19 (d, 1H, J = 5 Hz, H_{pyrr}), 9.17 (s, 1H, H_{pyrr}), 8.67 (d, 1H, J = 5 Hz, H_{pyrr}), 8.52 (d, 1H, J = 5 Hz, H_{pyrr}), 8.49 (d, 1H, J = 5 Hz, H_{pyrr}), 8.45 (dd, 1H, J = 7.6 and 1.5 Hz, H_{Phcycl}), 8.41 (d, 1H, J = 5 Hz, H_{pyrr}), 8.38 (d, 1H, J = 5 Hz, H_{pyrr}), 7.94 (dd, 1H, J = 7.6 and 1.5 Hz, H_{Phcycl}), 7.77−7.81 (m, 6H, $H_{o\text{-}Ar}$), 7.68 (ddd, 1H, J = 7.6 Hz, 7.6 and 1.5 Hz, H_{Phcycl}), 7.44 (ddd, 1H, J = 7.6 Hz, 7.6 and 1.5 Hz, H_{Phcycl}), 7.15−7.19 (m, 6H, $H_{m\text{-}Ar}$), 4.18 (m, 6H, O−CH_2), 1.92 (m, 6H, CH_2), 1.57 (m, 6H, CH_2), 1.26−1.48 (m, 48H, CH_2), 0.88−0.92 (m, 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 182.6, 159.4, 159.2, 159.1, 145.6, 145.1, 144.1, 143.6, 143.2, 141.1, 140.7, 139.6, 139.4, 135.5, 135.3, 134.6, 134.4, 134.3, 134.2, 133.7, 133.6, 132.9, 132.6, 132.5, 131.8, 131.7, 131.1, 127.4, 125.4, 121.5, 118.6, 113.3, 113.2, 108.6, 68.34, 68.31, 68.28, 31.97, 31.96, 29.75, 29.74, 29.73, 29.71, 29.70, 29.69, 29.68, 29.67, 29.53, 29.51, 29.44, 29.43, 29.42, 29.40, 26.21, 26.20, 22.74, 14.18. UV−vis (CH_2Cl_2): λ_{max} (ε) = 466 (108000), 650 (15000), 690 nm (9500sh $M^{-1}\cdot cm^{-1}$). Elem. Anal. Calcd for $C_{81}H_{98}N_4NiO_4\cdot H_2O$: C 76.7, H 7.95, N 4.42. Found: C 76.34, H 8.16, N 4.27.

Porphyrin ***3***. A solution of sodium hydroxide (900 mg, 22.5 mmol), 4-amino-4*H*-1,2,4-triazole (180 mg, 2.1 mmol), and nickel porphyrin **2** (223 mg, 0.178 mmol) in toluene/ethanol (120 mL/12 mL) was refluxed under argon for 1 h. After the mixture was cooled, the reaction medium is washed with water (600 mL). The organic phase is dried and the solvents evaporated. The solid residue was purified by

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Inorg. Chem. XXXX, XXX, XXX−XXX

column chromatography (silica gel, dichloromethane/cyclohexane, 1/1) and the nickel porphyrin **3** isolated in 92% yield after recrystallization from dichloromethane and methanol (210 mg, 0.166 mmol). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ_H 9.15 (d, 1H, J = 5 Hz, H_{pyrr}), 8.71 (d, 1H, J = 5 Hz, H_{pyrr}), 8.6 (very broad, NH), 8.54 (dd, 1H, J = 8 and 1.2 Hz, H_{Phcycl}), 8.48 (d, 1H, J = 5 Hz, H_{pyrr}), 8.41 (d, 1H, J = 5 Hz, H_{pyrr}), 8.32 (d, 1H, J = 5 Hz, H_{pyrr}), 8.30 (d, 1H, J = 5 Hz, H_{pyrr}), 8.11 (dd, 1H, J = 8 and 1.2 Hz, H_{Phcycl}), 7.81 (d, 2H, J = 8 Hz, $H_{o\text{-}Ar}$), 7.78 (d, 2H, J = 8 Hz, $H_{o\text{-}Ar}$), 7.72 (ddd, 1H, J = 8 Hz, 8 and 1.2 Hz, H_{Phcycl}), 7.69 (d, 2H, J = 8 Hz, $H_{o\text{-}Ar}$), 7.50 (ddd, 1H, J = 8 Hz, 8 and 1.2 Hz, H_{Phcycl}), 7.25 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.16 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.15 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 5.45 (very broad, NH), 4.18 (m, 6H, O−CH_2), 1.90−1.96 (m, 6H, CH_2), 1.56−1.60 (m, 6H, CH_2), 1.26−1.47 (m, 48H, CH_2), 0.88−0.92 (m, 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 180.9, 160.2, 159.9, 159.1, 159.0, 144.5, 143.9, 142.4, 141.5, 141.4, 141.1, 140.7, 139.3, 134.5, 134.2, 133.4, 132.4, 132.0, 131.9, 131.6, 129.3, 123.4, 119.5, 119.3, 115.0, 113.2, 113.1, 112.0, 102.6, 68.4, 68.28, 63.26, 31.97, 31.96, 29.74, 29.73, 29.70, 29.69, 29.67, 29.52, 29.51, 29.45, 29.43, 29.41, 29.40, 29.37, 26.21, 26.20, 26.19, 22.7, 14.2. UV−vis (CH_2Cl_2): λ_{max} (ε) = 464 (65000), 598 (7900), 650 nm (13600 $M^{-1}\cdot cm^{-1}$).

Porphyrin ***4***. A solution of nickel porphyrin **3** (200 mg, 0.158 mmol) and Lawesson's reagent (100 mg, 1.75 mmol) in benzene (100 mL) was refluxed under argon for 2 h. After evaporation of the solvent, the solid residue is purified by column chromatography (silica gel, dichloromethane/cyclohexane, 1/1). The desired compound **4** is isolated in 95% yield after recrystallization from dichloromethane and methanol (192 mg, 0.15 mmol). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ_H 12.27 (d, J = 4.8 Hz, NH), 9.09 (dd, 1H, J = 8 and 1.2 Hz, H_{Phcycl}), 9.08 (d, 1H, J = 5 Hz, H_{pyrr}), 8.66 (d, 1H, J = 5 Hz, H_{pyrr}), 8.42 (d, 1H, J = 5 Hz, H_{pyrr}), 8.36 (d, 1H, J = 5 Hz, H_{pyrr}), 8.26 (d, 1H, J = 5 Hz, H_{pyrr}), 8.23 (d, 1H, J = 5 Hz, H_{pyrr}), 8.07 (dd, 1H, J = 8 and 1.2 Hz, H_{Phcycl}), 7.66−7.80 (broad, 6H, $H_{o\text{-}Ar}$), 7.70 (ddd, 1H, J = 8 Hz, 8 and 1.2 Hz, H_{Phcycl}), 7.50 (ddd, 1H, J = 8 Hz, 8 and 1.2 Hz, H_{Phcycl}), 7.25 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.16 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.13 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 6.28 (d, J = 4.8 Hz, NH), 4.17 (m, 6H, O−CH_2), 1.90−1.96 (m, 6H, CH_2), 1.56−1.60 (m, 6H, CH_2), 1.26−1.47 (m, 48H, CH_2), 0.88−0.92 (m, 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 193.5, 164.1, 160.0, 159.2, 159.1, 144.4, 144.3, 142.9, 141.7, 141.2, 140.4, 138.9, 136.7, 134.8, 134.6, 134.4, 134.1, 132.2, 131.9, 131.8, 131.7, 131.6, 130.8, 130.7, 130.3, 130.0, 129.2, 128.9, 125.9, 124.0, 122.7, 120.7, 118.8, 115.4, 113.2, 113.1, 103.8, 68.4, 68.3, 68.2, 32.0, 31.9, 29.75, 29.73, 29.71, 29.69, 29.68, 29.67, 29.53, 29.51, 29.45, 29.43, 29.41, 29.40, 29.36, 26.21, 26.20, 22.74, 22.73, 14.2. UV−vis (CH_2Cl_2): λ_{max} (ε) = 426 (62500), 496 (89000), 688 nm (22900 $M^{-1}\cdot cm^{-1}$). Elem. Anal. Calcd for $C_{81}H_{99}N_5NiO_3S$: C 75.92, H 7.79, N 5.47. Found: C 75.69, H 7.92, N 5.30.

Porphyrin Dimer ***6***. A solution of porphyrin **4** (60 mg, 46.8 μmol) and $Pd(acac)_2$ (7 mg, 23 μmol) in 1,2-dichloroethane was heated at 80 °C under argon for 2 h. After the mixture was cooled and the solvent was evaporated, the solid residue was purified by column chromatography (cyclohexane/dichloromethane, 7/3). The ^{1}H NMR spectrum revealed the presence of two dimeric compounds (**5** + **6**). This mixture of isomers was isolated in "80% yield". A solution of this mixture (40 mg) in dichloroethane (30 mL) was then refluxed overnight under argon. After the mixture was cooled and the solvent was evaporated, the solid residue was recrystallized from hexane and methanol. Compound **6** (35 mg) was obtained in 88% yield from the mixture of isomers. ^{1}H NMR ($CDCl_3$, 50 °C, 400 MHz): δ_H 9.21 (d, 2H, J = 8 Hz, H_{Phcycl}), 8.98 (d, 2H, J = 5 Hz, H_{pyrr}), 8.60 (d, 2H, J = 5 Hz, H_{pyrr}), 8.44 (s, 2H, NH), 8.30 (d, 2H, J = 8 Hz, H_{Phcycl}), 8.30 (d, 2H, J = 5 Hz, H_{pyrr}), 8.28 (d, 2H, J = 5 Hz, H_{pyrr}), 8.16 (d, 2H, J = 5 Hz, H_{pyrr}), 8.05 (d, 2H, J = 5 Hz, H_{pyrr}), 7.81 (d, 4H, J = 8 Hz, $H_{o\text{-}Ar}$), 7.81 (dd, 2H, J = 8 and 8 Hz, H_{Phcycl}), 7.76 (d, 4H, J = 8 Hz, $H_{o\text{-}Ar}$), 7.75 (d, 4H, J = 8 Hz, $H_{o\text{-}Ar}$), 7.73 (dd, 2H, J = 8 and 8 Hz, H_{Phcycl}), 7.51 (d, 4H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.17 (d, 4H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.13 (d, 4H, J = 8 Hz, $H_{m\text{-}Ar}$), 4.29 (t, 4H, J = 6.8 Hz, O−CH_2), 4.16 (m, 8H, O−CH_2), 1.90−1.98 (m, 12H, CH_2), 1.21−1.60 (m, 108H, CH_2), 0.87−0.91 (m, 12H, CH_3), 0.83 (t, 6H, J = 7 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 166.0, 160.7, 159.1, 155.6, 146.8, 143.6, 143.3, 141.6, 140.0, 139.4, 138.8, 134.5, 134.2, 134.1, 133.9, 133.2, 132.3, 132.1, 131.9, 131.8, 130.9, 130.3, 129.7, 129.5, 129.0, 128.7, 128.6, 126.2, 125.4, 124.5, 124.41, 124.4, 122.7, 116.0, 114.6, 113.25, 113.16, 102.4, 68.6, 68.3, 68.2, 32.0, 31.9, 29.73, 29.72, 29.69, 29.68, 29.66, 29.64, 29.61, 29.52, 29.51, 29.45, 29.44, 29.41, 29.39, 29.39, 29.34, 26.21, 26.19, 26.1, 22.72, 22.66, 14.15, 14.11. UV−vis (CH_2Cl_2): λ_{max} (ε) = 350 (48000sh), 401 (92100), 450 (110000), 480 (87000), 520 (145000), 658 (35000), 690 (31000), 730 nm (32000 $M^{-1}\cdot cm^{-1}$).

Porphyrin ***7***. A solution of porphyrin **4** (50 mg, 39 μmol) in 1,2-dichloroethane (100 mL) was added dropwise to a solution of $Pd(acac)_2$ (238 mg, 720 μmol, 20 equiv) at 60 °C in 1,2-dichloroethane (200 mL) under argon over a period of 3 h. After the mixture was cooled and the solvent was evaporated, two compounds were isolated after column chromatography (silica gel, cyclohexane/dichloromethane, 7/3). Dimer **6** (18 mg, 34%) and porphyrin **7** (23 mg, 40%) were obtained pure after crystallization from hexane, dichloromethane and methanol. ^{1}H NMR ($CDCl_3$, 50 °C, 400 MHz): δ_H 9.17 (d, 1H, J = 8 Hz, H_{Phcycl}), 9.00 (d, 1H, J = 5 Hz, H_{pyrr}), 8.62 (d, 1H, J = 5 Hz, H_{pyrr}), 8.32 (d, 1H, J = 8 Hz, H_{Phcycl}), 8.31 (d, 1H, J = 5 Hz, H_{pyrr}), 8.29 (d, 1H, J = 5 Hz, H_{pyrr}), 8.17 (d, 1H, J = 5 Hz, H_{pyrr}), 8.04 (d, 1H, J = 5 Hz, H_{pyrr}), 8.04 (s, 1H, NH), 7.80 (d, 2H, J = 8 Hz, $H_{o\text{-}Ar}$), 7.79 (dd, 1H, J = 8 and 8 Hz, H_{Phcycl}), 7.75 (d, 2H, J = 8 Hz, $H_{o\text{-}Ar}$), 7.66 (d, 2H, J = 8 Hz, $H_{o\text{-}Ar}$), 7.58 (dd, 1H, J = 8 and 8 Hz, H_{Phcycl}), 7.25 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.17 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.13 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 5.41 (s, 1H, H_{acac}), 4.15 (m, 6H, O−CH_2), 2.09 (s, 3H, Me_{acac}), 2.07 (s, 3H, Me_{acac}), 1.88−1.95 (m, 6H, CH_2), 1.55−1.60 (m, 6H, CH_2), 1.26−1.47 (m, 48H, CH_2), 0.88−0.91 (m, 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 186.5, 186.4, 164.5, 160.0, 159.2, 153.7, 146.5, 143.7, 143.3, 141.6, 140.0, 138.95, 138.9, 134.8, 134.4, 134.2, 133.9, 133.4, 133.0, 132.7, 132.2, 131.8, 131.4, 130.9, 130.6, 129.9, 129.2, 129.1, 128.7, 128.5, 125.6, 124.6, 122.9, 115.5, 114.6, 113.3, 113.2, 102.4, 100.3, 68.29, 68.25, 68.1, 32.0, 29.72, 29.71, 29.70, 29.68, 29.66, 29.65, 29.53, 29.50, 29.49, 29.43, 29.42, 29.38, 26.9, 26.5, 26.3, 26.19, 26.18, 26.18, 22.7, 14.1. UV−vis (CH_2Cl_2): λ_{max} (rel. Abs.) = 356 (sh, 0.4), 390 (sh, 0.53), 410 (sh, 0.59), 434 (1), 467 (0.69), 497 (0.82), 648 (0.20), 672 (0.23), 704 nm (0.33).

Porphyrin Dimer ***9***. A solution of porphyrin **4** (70 mg, 55 μmol), porphyrin **8** (54 mg, 55 μmol), and $Pd(acac)_2$ (16.6 mg, 55 μmol) in 1,2-dichloroethane was heated at 80 °C under argon for 2 h. After the mixture was cooled and the solvent was evaporated, the complex mixture was purified by column chromatography (silica gel, cyclohexane/dichloromethane/toluene, 45/45/10). Several dimers were isolated after crystallization from hexane, dichloromethane and methanol: the mixture of dimers **5** and **6** (30 mg), dimer **9** (60 mg, 45%) and dimer **10** (22 mg, 19%). P Porphyrin **9**: ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ_H 9.27 (dd, 1H, J = 8 and 1.5 Hz, H_{Phcycl}), 9.25 (d, 1H, J = 5 Hz, H_{pyrr}), 9.16 (d, 1H, J = 5 Hz, H_{pyrr}), 9.15 (dd, 1H, J = 8 and 1.5 Hz, H_{Phcycl}), 9.01 (d, 1H, J = 5 Hz, H_{pyrr}), 8.63 (d, 1H, J = 5 Hz, H_{pyrr}), 8.53 (dd, 1H, J = 8 and 1.5 Hz, H_{Phcycl}), 8.44 (s, 1H, NH), 8.33 (dd, 1H, J = 8 and 1.5 Hz, H_{Phcycl}), 8.30 (d, 1H, J = 5 Hz, H_{pyrr}), 8.28 (d, 1H, J = 5 Hz, H_{pyrr}), 8.25 (dd, 1H, J = 8 and 1.5 Hz, H_{Phcycl}), 8.22 (t, 1H, J = 1.5 Hz, $H_{Ar\text{-}para}$), 8.16 (d, 1H, J = 5 Hz, H_{pyrr}), 8.12 (dd, 1H, J = 8 and 1.5 Hz, H_{Phcycl}), 8.08 (d, 1H, J = 5 Hz, H_{pyrr}), 8.02 (d, 1H, J = 5 Hz, H_{pyrr}), 7.67−7.89 (m, $4H_{Ar\text{-}ortho}$ + $1H_{pyrr}$ + $5H_{Phcycl}$ + $6H_{o\text{-}Ar}$), 7.57 (dd, 1H, J = 8 and 8 Hz, H_{Phcycl}), 7.51 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.17 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.13 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 4.29 (t, 2H, J = 7 Hz, O−CH_2), 4.16 (t, 2H, J = 7 Hz, O−CH_2), 4.14 (t, 2H, J = 7 Hz, O−CH_2), 1.89−1.99 (m, 6H, CH_2), 1.28−1.57 (m, 36H, H_{tBu} + 54H, −CH_2), 0.89−0.91 (m, 6H, −CH_3), 0.85 (t, 3H, J = 7 Hz, −CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 180.6, 166.0, 165.5, 163.0, 160.8, 159.2, 159.1, 158.0, 157.0, 155.7, 152.4, 152.0, 146.9, 143.7, 143.3, 141.7, 141.5, 141.2, 141.0, 140.0, 139.6, 139.4, 138.9, 138.4, 137.6, 136.0, 135.7, 134.8, 134.7, 134.5, 134.2, 134.1, 133.9, 133.7, 133.5, 133.2, 132.7, 132.2, 132.1, 131.9, 131.8, 131.6, 130.9, 130.5, 129.9, 129.8, 129.3, 129.2, 128.8, 128.7, 128.6, 127.3, 127.2, 126.8, 126.2, 125.0, 124.6, 122.8, 122.7, 122.6, 120.1, 116.1, 114.7, 113.3, 113.2, 111.4, 106.6, 103.1, 102.2, 96.1, 68.7, 68.3, 68.2, 53.4, 50.9, 35.4, 35.2, 31.95, 31.93, 31.7, 31.5, 29.75, 29.72, 29.69,

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Inorg. Chem. XXXX, XXX, XXX−XXX

29.66, 29.57, 29.50, 29.43, 29.39, 26.2, 26.19, 26.1, 22.72, 22.69, 14.15, 14.13. UV−vis (CH_2Cl_2): λ_{max} (ε) = 405 (80000), 445 (87000), 478 (89700), 503 (84000), 575 (105000), 646 (38000), 682 (32000), 728 (29000), 799 nm (13700 $M^{-1}\cdot cm^{-1}$).

Porphyrin Dimer ***10***. ^1H NMR ($CDCl_3$, 25 °C, 400 MHz): δ_H 9.24 (dd, 2H, J = 8 and 1 Hz, H_{Phcycl}), 9.23 (d, 2H, J = 5 Hz, H_{pyrr}), 9.19 (d, 2H, J = 5 Hz, H_{pyrr}), 8.53 (dd, 2H, J = 8 and 1 Hz, H_{Phcycl}), 8.28 (dd, 2H, J = 8 and 1 Hz, H_{Phcycl}), 8.22 (t, 2H, J = 1.8 Hz, H_{para}), 8.14 (dd, 2H, J = 8 and 1 Hz, H_{Phcycl}), 8.12 (s, 2H, NH), 8.09 (d, 2H, J = 4.8 Hz, H_{pyrr}), 7.87 (ddd, 2H, J = 8 Hz, 8 and 1 Hz, H_{Phcycl}), 7.87 (d, 2H, J = 4.8 Hz, H_{pyrr}), 7.79 (ddd, 2H, J = 8 Hz, 8 and 1 Hz, H_{Phcycl}), 7.74 (t, 2H, J = 1.8 Hz, H_{para}), 7.72 (ddd, 2H, J = 8 Hz, 8 and 1 Hz, H_{Phcycl}), 7.56 (ddd, 2H, J = 8 Hz, 8 and 1 Hz, H_{Phcycl}),, 1.54 (s, 18H, H_{tBu}), 1.41 (s, 18H, H_{tBu}). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): extremely low solubility (only C−H and CH_3 were observed) δ_C 134.4, 134.1, 133.2, 133.0, 131.3, 129.4, 129.2, 128.5, 128.4, 126.8, 126.7, 125.2, 122.3, 122.2, 31.2, 31.0. UV−vis (CH_2Cl_2): λ_{max} (rel. abs.) = 360 (0.36), 412 (0.46), 482 (0.54), 550 (0.47sh), 590 (1), 638 (0.35), 690 (0.19), 720 (0.17), 798 nm (0.16).

Porphyrin Dimer ***11***. A solution of porphyrin dimer **9** (50 mg, 21 μmol) and Lawesson's reagent (48 mg, 0.12 mmol) in freshly distilled toluene (150 mL) was heated at 80 °C under argon for 1 h. After it was cooled, the mixture was purified by column chromatography (silica gel, cyclohexane/dichloromethane, 8/2) and porphyrin dimer **11** (28 mg, 56%) was isolated together with recovered starting material **9** (8 mg, 16%) and different monomeric porphyrins. ^1H NMR ($CDCl_3$, 25 °C, 500 MHz): δ_H 11.48 (d, 1H, J = 5 Hz, NH), 9.24 (dd, 1H, J = 8 and 1.5 Hz, H_{Phcycl}), 9.17 (d, 1H, J = 5 Hz, H_{pyrr}), 9.14 (dd, 1H, J = 8 and 1.5 Hz, H_{Phcycl}), 9.13 (d, 1H, J = 5 Hz, H_{pyrr}), 9.06 (dd, 1H, J = 8 and 1.5 Hz, H_{Phcycl}), 8.99 (d, 1H, J = 5 Hz, H_{pyrr}), 8.61 (d, 1H, J = 5 Hz, H_{pyrr}), 8.41 (s, 1H, NH), 8.31 (d, 1H, J = 8 Hz, H_{Phcycl}), 8.26 (d, 1H, J = 5 Hz, H_{pyrr}), 8.25 (d, 1H, J = 5 Hz, H_{pyrr}), 8.24 (d, 1H, J = 8 Hz, H_{Phcycl}), 8.21 (t, 1H, J = 1.5 Hz, $H_{Ar\text{-}para}$), 8.13 (d, 1H, J = 5 Hz, H_{pyrr}), 8.09 (d, 1H, J = 8 Hz, H_{Phcycl}), 8.08 (s, 1H, NH), 8.03 (d, 1H, J = 5 Hz, H_{pyrr}), 7.99 (d, 1H, J = 5 Hz, H_{pyrr}), 7.85 (d, 1H, J = 5 Hz, H_{pyrr}), 8.04 (s, 1H, NH), 7.67−7.88 (m, $4H_{Ar\text{-}ortho}$ + $1H_{Ar\text{-}para}$ + $5H_{Phcycl}$ + $6H_{o\text{-}Ar}$), 7.55 (ddd, 1H, J = 8 Hz, 8 and 1.5 Hz, H_{Phcycl}), 7.49 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.15 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.11 (d, 2H, J = 8 Hz, $H_{m\text{-}Ar}$), 5.77 (d, 1H, J = 5 Hz, NH), 4.27 (t, 3H, J = 6.5 Hz, O−CH_2), 4.15 (t, 3H, J = 6.5 Hz, O−CH_2), 4.12 (t, 3H, J = 6.5 Hz, O−CH_2), 1.87−1.96 (m, 6H, CH_2), 1.24−1.60 (m, 36H, H_{tBu} + 54H, −CH_2), 0.85−0.89 (m, 6H, CH_3), 0.83 (t, 3H, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 194.6, 166.0, 165.2, 161.9, 160.8, 159.2, 159.1, 157.1, 155.6, 152.4, 146.9, 144.1, 143.7, 143.3, 141.7, 140.8, 140.2, 140.0, 139.9, 139.4, 139.2, 138.9, 137.8, 137.1, 135.8, 135.6, 134.8, 134.7, 134.5, 134.3, 134.2, 134.0, 133.9, 133.9, 133.7, 133.3, 133.2, 133.0, 132.8, 132.2, 132.1, 131.9, 131.8, 131.7, 130.9, 130.7, 130.5, 130.4, 129.8, 129.4, 129.2, 128.8, 128.7, 128.5, 127.4, 127.1, 126.9, 126.4, 126.2, 126.1, 124.9, 124.8, 124.7, 122.9, 122.8, 122.8, 122.6, 120.6, 116.1, 114.7, 113.3, 113.2, 107.5, 103.9, 102.1, 68.7, 68.3, 68.2, 35.4, 35.3, 31.95, 31.93, 31.7, 31.5, 29.75, 29.72, 29.71, 29.70, 29.69, 29.67, 29.66, 29.65, 29.57, 29.51, 29.50, 29.43, 29.39, 26.20, 26.19, 26.09, 22.72, 22.69, 14.15, 14.13. UV−vis (CH_2Cl_2): λ_{max} (ε) = 365 (67000), 403 (79000sh), 425 (90000sh), 443 (104000), 483 (81000), 509 (105000), 607 (98700), 658 (50200), 727 (36600), 840 nm (14400 $M^{-1}\cdot cm^{-1}$).

Porphyrin Dimer ***12***. A solution of porphyrin dimer **10** (110 mg, 53 μmol) and Lawesson's reagent (200 mg, 0.5 mmol) in freshly distilled toluene (100 mL) was refluxed under argon for 1 h. After it was cooled, the mixture was passed through a short alumina column to eliminate the precipitated Lawesson reagent. After evaporation of the solvent, porphyrin dimer **12** (102 mg, 91%) was isolated by crystallization from *n*-hexane, dichloromethane and methanol. ^1H NMR ($CDCl_3$, 25 °C, 500 MHz): δ_H 11.50 (d, 2H, J = 5 Hz, NH), 9.25 (dd, 2H, J = 8 and 1.5 Hz, H_{Phcycl}), 9.22 (d, 2H, J = 5 Hz, H_{pyrr}), 9.19 (d, 2H, J = 5 Hz, H_{pyrr}), 9.09 (dd, 2H, J = 8 and 1.5 Hz, H_{Phcycl}), 8.32 (dd, 2H, J = 8.0 and 1.5 Hz, H_{Phcycl}), 8.24 (t, 2H, J = 1.8 Hz, H_{para}), 8.12 (s, 2H, NH), 8.11 (dd, 2H, J = 8.0 and 1.5 Hz, H_{Phcycl}), 8.08 (d, 2H, J = 5 Hz, H_{pyrr}), 7.90 (d, 2H, J = 4.7 Hz, H_{pyrr}), 7.91 (ddd, 2H, J = 8 Hz, 7 and 1.5 Hz, H_{Phcycl}), 7.83 (ddd, 2H, J = 8 Hz, 7 and 1.5 Hz, H_{Phcycl}), 7.78 (t, 2H, J = 1.8 Hz, H_{para}), 7.72 (ddd, 2H, J = 8 Hz, 7 and 1.5 Hz, H_{Phcycl}), 7.58 (ddd, 2H, J = 8 Hz, 7 and 1.5 Hz, H_{Phcycl}), 5.81 (d, 2H, J = 5 Hz, NH), 1.55 (s, 18H, ^tBu), 1.44 (s, 18H, ^tBu). ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz): δ_C 194.6, 165.1, 161.9, 157.0, 152.4, 144.0, 140.6, 140.2, 139.9, 139.2, 137.8, 137.1, 135.8, 135.6, 134.9, 134.2, 133.9, 133.8, 133.1, 132.4, 132.2, 130.7, 129.5, 128.5, 127.4, 126.1, 126.1, 122.5, 120.5, 107.5, 103.8, 35.4, 35.3, 31.7, 31.5. UV−vis (CH_2Cl_2): λ_{max} (rel. Abs.) = 341 (0.48), 362 (0.51), 429 (0.64), 463 (0.49), 506 (0.51), 619 (1), 659 (0.49), 718 (0.32), 765 (0.25sh), 841 nm (0.25).

Porphyrin Trimer ***14***. A solution of porphyrin **7** (10 mg, 7 μmol) and porphyrin **13** (3.5 mg, 3.5 μmol) in 1,2-dichloroethane (20 mL) was heated at 60 °C under argon for 1 h. After the mixture was cooled and the solvent was evaporated, the trimeric compound **14** was purified by gel permeation chromatography (biobeads S-X1, dichloromethane) and isolated in 77% yield (10 mg, 2.6 μmol). ^1H NMR ($CDCl_3$, 50 °C, 400 MHz): δ_H 9.28 (d, 2H, J = 8 Hz, H_{Phcycl}), 9.23 (s, 2H, H_{pyrr}), 9.20 (d, 2H, J = 8 Hz, H_{Phcycl}), 9.02 (d, 2H, J = 5 Hz, H_{pyrr}), 8.62 (d, 2H, J = 5 Hz, H_{pyrr}), 8.47 (s, 2H, NH), 8.35 (d, 2H, J = 8 Hz, H_{Phcycl}), 8.34 (d, 2H, J = 8 Hz, H_{Phcycl}), 8.30 (d, 2H, J = 5 Hz, H_{pyrr}), 8.28 (d, 2H, J = 5 Hz, H_{pyrr}), 8.24 (t, 2H, J = 1.5 Hz, $H_{Ar\text{-}para}$), 8.17 (d, 2H, J = 5 Hz, H_{pyrr}), 8.03 (s, 2H, NH), 8.02 (d, 2H, J = 5 Hz, H_{pyrr}), 7.88 (s, 2H, H_{pyrr}), 7.74−7.88 (m, $8H_{Phcycl}$ + $8H_{Ar\text{-}ortho}$ + $12H_{o\text{-}Ar}$), 7.52 (d, 4H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.18 (d, 4H, J = 8 Hz, $H_{m\text{-}Ar}$), 7.14 (d, 4H, J = 8 Hz, $H_{m\text{-}Ar}$), 4.32 (t, 4H, J = 7 Hz, O−CH_2), 4.17 (m, 8H, O−CH_2), 1.90−2.01 (m, 12H, CH_2), 1.27−1.57 (m, $36H_{tBu}$ + $108H_{CH2}$), 0.89−0.92 (m, 12H, CH_3), 0.86 (t, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C 166.0, 164.6, 160.8, 159.2, 159.1, 156.4, 155.8, 152.2, 146.9, 143.7, 143.3, 141.7, 140.0, 139.44, 139.38, 138.9, 137.6, 135.8, 134.7, 134.5, 134.2, 134.1, 133.9, 133.7, 133.2, 133.1, 132.1, 132.0, 131.8, 131.4, 130.9, 130.5, 129.8, 129.2, 128.8, 128.7, 127.5, 126.6, 126.4, 126.2, 125.0, 124.6, 122.8, 121.3, 116.1, 114.6, 113.3, 113.2, 105.2, 102.2, 68.7, 68.29, 68.26, 35.4, 31.9, 31.7, 29.8, 29.7, 29.71, 29.70, 29.68, 29.66, 29.58, 29.51, 29.44, 29.39, 26.2, 26.1, 22.72, 22.70, 14.1. UV−vis (CH_2Cl_2): λ_{max} (ε) = 405 (117000), 456 (144000), 480 (133000sh), 514 (158600), 620 (99200), 680 (78000), 730 (61000), 812 (9700), 426 (62500), 913 nm (21000 $M^{-1}\cdot cm^{-1}$).

X-ray Crystallography. *Crystal Data* ***8***. X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Cu−Kα radiation (λ = 1.54178 Å). The crystal-detector distance was 40 mm. The cell parameters were determined (APEX2 software)[18] from reflections taken from tree sets of 20 frames, each at 10 s exposure. The structure was solved by Direct methods using the program SHELXS-2013.[19] The refinement and all further calculations were carried out using SHELXL-2013.[20] The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F2. A semiempirical absorption correction was applied using SADABS in APEX2 ; transmission factors: T_{min}/T_{max} = 0.6231/0.7528. The SQUEEZE instruction in PLATON[21] was applied. The residual electron density was assigned to half a molecule of chlorobenzene. $C_{62}H_{58}N_6NiOS$, M = 993.91 $g\cdot mol^{-1}$, black prism, monoclinic, space group $C2/c$, a = 23.3114(6) Å, b = 14.1663(4) Å, c = 34.3124(10) Å, α = 90°, β = 90.3370(10)°, γ = 90°, V = 11331.0(5) $Å^3$, $\rho_{calc.}$ = 1.165 $g\cdot cm^{-3}$, Z = 8, T = 173 K, 3.792 < θ < 66.6, transmission factors T_{min}/T_{max} = 0.6231/0.7528, 54991 reflections measured, 9895 unique reflections, R_1 = 0.064, R_2 = 0.1693, GOF = 1.062. CCDC number: 1573335.

Crystal Data ***12***. Transmission factors: T_{min}/T_{max} = 0.4866/0.7528. The SQUEEZE instruction in PLATON was applied. The residual electron density was assigned to a molecule of chlorobenzene. The atoms C104, C105, and C106 are disordered over two positions with an occupancy ratio of 0.7/0.3. $C_{154}H_{139}Cl_5N_{12}Ni_2PdS_4$, M = 2687.07 $g\cdot mol^{-1}$, black plate, monoclinic, space group $P21/c$, a = 20.6340(8) Å, b = 26.9516(16) Å, c = 28.2022(13) Å, α = 90°, β = 112.533(3)°, γ = 90°, V = 14486.5(13) $Å^3$, ρ_{calcd} = 1.232 $g\cdot cm^{-3}$, Z = 4, T = 130(2) K, 4.0 < θ < 66.622. Transmission factors: T_{min}/T_{max} = 0.4866/0.7528, 109226 reflections measured, 25034 unique reflections, R_1 = 0.1637, R_2 = 0.4055, GOF = 1.200. CCDC number: 1573332.

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Inorg. Chem. XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02422.

Spectral data (^{1}H and ^{13}C NMR, MALDI mass spectra, UV−visible) of all new compounds (PDF)

Accession Codes

CCDC 1573332 and 1573335 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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